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(54) Title: POLYCYANOACRYLATE FOAM

(57) Abstract

Polycyanoacrylate foam is made by mixing together a cyanoacrylate monomer, a liquid foaming agent and a polymerisation initiator. The mixture simultaneously polymerises and foams. The foaming agent is usually an organic compound with a boiling point not higher than 100 °C, miscible with the monomer but not a solvent for the polymer. The monomer may be any 2-cyanoacrylate ester compatible with the composition.

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POLYCYANOACRYLATE FOAM

This invention relates to a foam forming cyanoacrylate composition.

Since their commercialization in the sixties adhesives based on cyanoacrylate monomers have found wide application. Numerous compositions are known in the art. A variety of additional components are introduced into the cyanoacrylate monomer to impart thickening (US Patent No. 2,794,788) and thixotropy (US Patent No. 4,533,422) of the adhesive, toughness (WO 83/02,450), heat resistance (Japanese Patent No. 62,199,668), impact and peel-resistance (Japanese Patent No. 63,00,377), electroconductivity (WO 86/06,738) and other properties of the resultant adhesive bond.

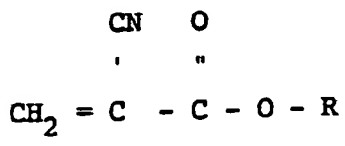
It has now been unexpectedly found that when cyanoacrylate monomers are mixed with organic liquids and polymerization initiators the so formed composition can transform itself by simultaneous polymerization and expansion into a polycyanoacrylate foam.

The present invention provides cyanoacrylate based composition, comprising a cyanoacrylate monomer, a liquid foaming agent and a cyanoacrylate polymerization initiator.

Upon or after formation of the composition it polymerizes to produce expanded polycyanoacrylate foam. The composition can also optionally contain other reactive monomers, as well as modifiers and additives such as polymeric thickeners, plasticizers, thixotropic agents, compatibilizers, pigments and colourants, fillers, deodorants and perfumes, for example.

In another aspect the invention provides a method of creating a polycyanoacrylate foam and the foam itself.

The cyanoacrylate monomers used in the composition of the invention are 2-cyanoacrylate esters of the formula



wherein R represents an ester-forming group. In principle, R can be any ester-forming group compatible with the monomer and with foam formation. For example, the group R should not initiate autopolymerization of the monomer or prevent polymerization of the composition described above. R should also desirably be selected to provide a foam with the desired properties.

Preferably R represents alkyl, alkenyl, alkynyl, aryl or an aromatic heterocyclic radical. R may also be one of the foregoing moieties substituted with one or more other of the moieties; this includes the case of a substituent itself being substituted. Group R may contain other compatible substituents, for example alkoxy, alkoxyalkoxy, carbalkoxyalkyl or halogen. In general, R can be any moiety which does not contain a sufficiently nucleophilic group to initiate polymerization or sufficiently electrophilic group to interfere with polymerization. The alkyl or alkenyl moiety may be cyclic and normally R contains from 1 to 16 carbon atoms and often is a 1C, 2C, 3C, 4C, 5C, 6C, 7C or 8C group, more usually it is a 1C-6C group. In the case of

moieties containing a heterocycle, heteroatom ring members are normally counted as a carbon atom.

More preferably, R is alkyl, halogenated alkyl, alkenyl, alkynyl, phenyl, halogenated phenyl, phenylalkyl, halogenated phenylalkyl, alkoxyalkyl, alkoxyalkoxyalkyl, carbalkoxymethyl or alkylideneglyceryl, wherein the terms "alkyl" and "alkenyl" include the corresponding cyclic radicals. Uninterrupted carbon chains preferably contain 1, 2 or 3 carbon atoms.

Specific examples of R are methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, pentyl, hexyl, trifluoroethyl, 2-chloroethyl, 3-chloropropyl, 2-chlorobutyl, cyclohexyl, tertiary butylcyclohexyl, benzyl, phenyl, cresyl, allyl, crotyl, methallyl, propargyl, furfuryl, 2-methoxyethyl, 2-ethoxyethyl, 2-methoxyisopropyl, 2-(2'-ethoxy)-ethoxymethyl, 2-(2'-ethoxy)-ethoxyethyl, 2-(2'-ethoxy)-ethoxybutyl, methoxycarbonylmethyl, ethoxycarbonylmethyl, isopropoxycarbonylmethyl, isobutoxycarbonylmethyl, isoamyloxycarbonylmethyl and 1,2-isopropylideneglyceryl. Most preferred are ethyl, n-butyl, iso-butyl, 2-methoxyethyl, 2-ethoxyethyl and 2-methoxyisopropyl cyanoacrylates.

If desired, a mixture of two or more cyanoacrylate monomers may be used.

Usually the cyanoacrylate monomers are stabilized with anionic and free-radical polymerization inhibitors. Anionic polymerization inhibitors known in the art are soluble acidic gases (for example sulfur dioxide), hyrogen fluoride, phosphonic, carboxylic and organic sulfonic acids,

sultones, BF_3 and its complexes and phosphazenes, for example. The free-radical polymerization inhibitors are usually hydroquinone, p-methoxyphenol or t-butyl catechol, for example.

The inhibitors are normally used in small amounts of from 0.00001 to 1% by weight of the monomer. The preferred quantities for the above-mentioned inhibitors are: acidic gases - from 0.001% to 0.06%; acids - from 0.0005% to 0.01%; sultones - from 0.01% to 0.1%; BF_3 - from 0.0001% to 0.01%; phosphazenes - from 0.0001% to 0.001%; free-radical inhibitors - from 0.001% to 1%. The foregoing percentages are percentages by weight of the cyanoacrylate monomer. It should be noted that the quantity of inhibitor will influence the onset of polymerization of the composition of the present invention and could be used as a means to control the time interval between the formation of the composition and its transformation into a polymeric cyanoacrylate foam.

The liquid foaming agent used in the composition of the present invention can be any organic compound with a boiling point preferably not higher than 100°C. The liquid foaming agent used can be a single compound or a mixture thereof. Preferably it will be soluble or semi-soluble in the cyanoacrylate monomer and will not act as a solvent for the corresponding polycyanoacrylate. Preferably its solubility parameter should be below 9. Preferably it is a non-polar liquid. Preferably it should be non-toxic, non-flammable and non-irritant.

Solubility parameter is a quantity used to predict the solubility of solutes and solvents and is explained in the "CRC Handbook of Chemistry and Physics", published by CRC Press Inc. of Boca Raton, Florida, USA see for example page C-676 of the 67th Edition (1986-87). The CRC Handbook also contains lists of solubility parameter values.

Specific examples of foaming agents are pentane, hexane, heptane, 1,1,2-trichlorotriflouroethane, 1,1,1-trichlorotrifluoroethane, petroleum ether, diethyl ether, cyclopentane, cyclohexane, benzene, carbon tetrachloride, chloroform, methylcyclopentane, dimethylsulfide, 1,1-dichlororethane, 1,1,1-trichloroethane, perfluorohexane, perfluoroheptane, 1-bromopropane. Most preferred are pentane, hexane, 1,1,2-trichlorotriflouroethane, cyclohexane, petroleum ether and diethyl ether. The above-mentioned compounds are only representative and do not limit the compounds that can be used as liquid blowing agents. It was found that even very polar liquids like ethanol and methanol or liquids which are typical solvents for polycyanoacrylates, like acetone, 2-butanone and acetonitrile, can be used as foaming agents.

When solvents for polycyanoacrylates are used as foaming agents, they expand the foam but immediately thereafter the foam shrinks in volume or sometimes collapses. Such solvents are therefore normally unacceptable as foaming agents when used alone, but in principle can be used so long as the selected combination of solvent, polycyanoacrylate and their relative quantities do not lead to collapse of the foam. Polycyanoacrylate solvents are more acceptable when used in minor amounts with other foaming agents.

The volume ratio of cyanoacrylate monomer to foaming agent is not critical but is preferably from 1:10 to 20:1, more preferably from 1:2 to 5:1, especially from 1:1 to 4:1.

The cyanoacrylate polymerization initiator used in the composition of the present invention may comprise any of the known initiators and accelerators of the anionic polymerization of cyanoacrylate monomers, for example. The anionic initiator can be used singly or in admixture with one or more other initiators.

Specific examples of anionic initiators are pyridine, aminopyridine, vinylpyridine, methoxyethylpyridine, piperidine, picoline, lutidine, N,N-dimethyl-p-toluidine, N,N-dimethyl-o-toluidine, N,N-dimethyl-m-toluidine, triphenylphosphine, triethylphosphine, tribenzylamine, triethylamine, benzyldimethylamine, diethylenetriamine, benzyltriethylamine, tribenzylamine, poly(4-vinylpyridine), calixarenes, tertiary amine-SO_3 complexes, polyethyleneglycol, phenolformaldehyde resins, vinylimidazole, triethanolaminatotitanium, aminosilanes, phosphites, metal acetylacetonates, N-(oxydiethylene) benzothiazole-2-sulfenamide, bismuth dimethyldithiocarbamate, as well as alcohols, bases and hydroxyl or amine group containing compounds. Most preferred anionic polymerization initiators are N,N-dimethyl-p-toluidine and N-(oxydiethylene) benzothiazole-2-sulfenamide.

The above-mentioned compounds are only representative and do not restrict the scope of suitable initiators. For example any of the anionic polymerization initiators known in the

art for cyanoacrylate monomers or accelerators of their anionic polymerization can successfully be used in the compositions of the present invention. Optionally, but not necessarily, free-radical polymerization initiators such as methylethylketone peroxide, cyclohexane peroxide, cumene hydroperoxide or dibenzoyl peroxide, for example, can be used in conjunction with the anionic polymerization initiator.

In order to impart desired properties to the composition of the present invention and to the properties of the resultant foam, as well as for economic considerations, further additives can be introduced into the composition. They can be, for example, any of the known polymeric thickeners and viscosity regulators, rubbers, plasticizers and toughening, compatibilizers, thioxtropic agents, colourants, deodorants or perfumes, for example, used in cyanoacrylate adhesives.

The composition may also contain other monomers containing a reactive double bond, for example (di)acrylates or (di)methacrylates, or reactive resins or oligomers, e.g. epoxy or urethane, in minor amounts, e.g. up to 25 mole % of the total monomer content and more preferably in an amount of no more than 5 or 10 mole %.

Upon mixing the three major components of the present invention (monomer, foaming agent and initiator) a mixture is formed in which, under the action of the anionic initiator, polymerization of the cyanoacrylate monomer occurs. It is fast and exothermic, which leads to the simultaneous evaporation of the liquid foaming agent. As a result polycyanoacrylate foam is produced. The expanded material can occupy a volume of as much as 40 times the

volume of the original liquid composition. The expansion coefficient and the properties of the foam are dependent on the components used and their ratios. They are also dependent on the availabile volume for expansion. The formed polymeric foam is of a closed-cell type.

A distinctive feature is that the foam is covered by a thin film of polycyanoacrylate, which resembles a polycyanoacrylate glue-line and ensures excellent adhesion of the foam to the surface(s) which it has contacted. The time necessary for the onset of polymerization and foaming can be regulated from seconds to minutes by varying the type and amount of anionic initiator and/or stabilizer present in the cyanoacrylate monomer or composition.

Another distinctive feature of the composition of the present invention is that it is easy to prepare, the foaming reaction takes place at room temperature and compressed gases are not required or utilized.

Another distinctive feature of the foamed polycyanoacrylate is that it can easily be collapsed when contacted with solvents for polycyanoacrylates like acetone, acetonitrile, methylenechloride, N,N-dimethylformamide, nitromethane, butyrolactone or alkyl cyanoacetates, for example.

Applications of the foaming composition of the present invention and the method of obtaining polycyanoacrylate foams include two major areas, i.e. plugging of ducts, pipes and vessels and, secondly, adhesive bonding and sealing of porous substrates.

Using the foaming composition of the present invention temporary, permanent or semi-permanent blocking of flow of fluids in pipelines can be achieved. Gas and oil pipelines are of particular interest. Following repairs or other work on the pipeline the foam blockage can easily be collapsed by application of a suitable solvent. The main advantage of the material and method of the invention is the simplicity and speed of forming the foam, its high adhesion to the walls of the pipe, and the simplicity and speed of collapsing the foam.

Using the foaming composition of the present invention blood vessel occlusion, fallopian tube sealing or other medical or surgical procedures can be achieved. The above-mentioned applications are currently executed with conventional cyanoacrylates for the purpose of stopping haemorrhage and for female sterilization. Using the foaming composition in those cases would greatly increase the success rate of the present methods, ensuring excellent plugging capacity as a result of polymer expansion in the vessel. Furthermore the quantity of the cyanoacrylate introduced into the body will be reduced more than tenfold, which would greatly increase the physiological safety of the procedures.

Using the foaming composition of the present invention orthopaedic casts for broken limbs can be prepared. The distinct advantages will be the speed and ease of preparation of the casts, their extremely low weight and sufficient rigidity, advantages specially valuable in emergency cases and military action.

The cyanoacrylate monomer and the initiator must obviously be kept separate until it is desired to form the foaming composition, but the foaming agent may if desired be mixed with one or other (or both) of the monomer and the initiator to form a preblend.

It is therefore convenient to provide a binary delivery system holding the monomer and the initiator in separate containers from which they may be dispensed and mixed. If desired, the binary system could include a third container containing all or part of the foaming agent, and if desired separate containers holding other components may be provided. Such a binary or multipart delivery system forms one aspect of the invention.

The delivery system or kit may take the form of a syringe having an in-line static (stationary phase) mixer or of spray apparatus. In any event, it preferably includes means to mix the components prior to, or in the process of, their dispensing from the apparatus. In the case of a syringe, a thickener is preferably provided to increase the viscosity of the final composition.

Preferably, the delivery system is a two-part system, in which all the components are included in the containers holding the monomer preparation and the initiator.

The invention includes a preblend for forming the foaming composition, comprising the monomer and a foaming agent.

The above-mentioned applications are only indicative and do not limit the scope or application of the foaming composition of the present invention.

The invention is illustrated by the following examples.

Example 1

In an open polyethylene cylindrical container with a diameter of 50 mm, 4 ml of pure, freshly distilled ethyl 2-cyanoacrylate are placed. To the cyanoacrylate is added a given amount of liquid foaming agent, containing N,N-dimethyl-p-toluidine. The contents are manually mixed for 3 seconds so that a clear solution is produced. The so formed composition is left static and the time lapse before the onset of expansion and the time interval of actual expansion is recorded. The volume of the expanded foam is measured and the coefficient of expansion is calculated as the ratio of the volume of the polycyanoacrylate foam to the volume of the cyanoacrylate monomer in the composition. The results are shown in Table 1.

In Table 1, the concentration of initiator is expressed as percentage by weight based on the total composition.

Table 1

Foaming compositions based on different foaming agents (FA)

Foaming agent	Volume ratio of cyanoacrylate to FA	Concentr. of initiator wt.%	Solubility parameter of FA	Polarity of FA	b.p. of FA °C	Onset time sec	Time of expansion sec	Expansion coefficient
Pentane	1:1	0.025	7.0	non	35	20	5	23
Hexane	2:1	0.017	7.3	non	69	25	5	13
1,1,2-trichlorotrifluoroethane	4:1	0.010	7.3	non	48	6	6	25
Heptane	4:1	0.020	7.4	non	98	10	10	4
Diethyl ether	4:1	0.010	7.4	mod	35	19	5	18
Cyclohexane	2:1	0.017	8.2	non	81	34	5	10
2-Butanone	2:1	0.017	9.3	mod	80	10	15	17
Acetone	2:1	0.017	9.9	mod	56	5	10	22 *
Ethanol	2:1	0.017	10.0	high	78	5	10	10
Acetonitrile	2:1	0.017	11.9	high	82	10	10	3
Methanol	4:1	0.020	14.5	high	65	5	25	8

*Foam collapses after expansion

The ratio of ethyl 2-cyanoacrylate monomer to foaming agent in Table 1 was established to be the best for each pair in previous experiments. The results indicate that the most important factor in choosing the foaming agent is its boiling point and as can be seen the lower the boiling point the higher is the expansion which can be achieved. The following major consideration is the polarity and the solubility parameter of the foaming agent. Best results are produced with non-polar solvents with solubility parameters at the lower end of the scale, e.g. pentane, 1,1,2-trichlorotrifluoroethane. Foaming agents with solubility parameters at the other end of the scale and high polarity are normally unsuitable due to the formation of exceptionally brittle foams. Foaming agents with a solubility parameter similar to poly(ethyl 2-cyanoacrylate) and thus being good solvents for the foam, e.g. acetone, are also unsatisfactory due to immediate shrinkage and collapse of the foamed material. Solvents in the mid-range of the solubility parameter scale and with boiling point around 80°C, like cyclohexanone, produce resilient foams.

Example 2

Experiments according to the procedure described in Example 1 were carried out. Ethyl 2-cyanoacrylate was used as the cyanoacrylate monomer and 1,1,2-trichlorotrifluoroethane as the foaming agent. Different anionic polymerization initiators were evaluated. The ratio of cyanoacrylate to 1,1,2-trichlorotrifluoroethane and the concentration levels of the initiators were optimized in previous experiments. The results are presented in Table 2.

Table 2

Foaming compositions based on different anionic polymerization initiators (API)

API	Concentration of API in composition	Volume ratio of cyanoacrylate to foaming agent	Onset time	Time of expansion	Expansion coefficient
	wt.%		sec	sec	
N,N-Dimethyl-p-toluidine	0.010	4:1	6	6	25
Pyridine	0.0002	4:3	450	20	5
Piperidine	0.010	2:1	30	10	18
Triethyl phosphine	0.003	2:1	133	40	17
Triphenyl phosphine	0.0048	4:3	298	68	4
N-(oxydiethylene) benzothiazole-2-sulfenamide	0.017	2:1	25	5	25

The results summarized in Table 2 show that best expansion coefficients and time of expansion are achieved with N,N-dimethyl-p-toluidine and N-(oxydiethylene)benzothiazole-2-sulfenamide, the latter having the advantage of no odour. Piperidine gives slightly longer onset times and is very smelly. Very slow onset and expansion times can be achieved with triethylphosphine and triphenylphosphine.

Example 3.

Experiments according to the procedure described in Example 1 were carried out. Ethyl 2-cyanoacrylate was used as the cyanoacrylate monomer. 1,1,2-Trichlorotrifluoroethane was used as foaming agent. Their ratio was 4:1 by volume. N,N-dimethyl-p-toluidine was used as initiator in 0.01% by weight of the composition. The cyanoacrylate monomer was stabilized with p-toluenesulfonic acid or trifluoromethanesulfonic acid. The results of the onset time of foaming are presented in Table 3.

Table 3

Stabilized foaming compositions

Acid	Concentration of acid in cyanoacrylate wt.%	Onset time sec
p-Toluenesulfonic	0	10
p-Toluenesulfonic	0.0003	14
p-Toluenesulfonic	0.0006	16
p-Toluenesulfonic	0.0012	20
p-Toluenesulfonic	0.002	37
p-Toluenesulfonic	0.005	66
p-Toluenesulfonic	0.01	195
Trifluoro-methanesulfonic	0	10
Trifluoro-methanesulfonic	0.001	11
Trifluoro-methanesulfonic	0.002	24
Trifluoro-methanesulfonic	0.005	43
Trifluoro-methanesulfonic	0.01	117

The results presented in Table 3 clearly demonstrate that the introduction of sulfonic acids, which are often used commercially to stabilize the cyanoacrylate monomers, can increase the onset time of foam expansion and by regulating their level the period between mixing the composition of the present invention and its expansion into polymer foam can be controled.

Example 4

Experiments according to the procedure described in Example 1 were carried out. Different types of cyanoacrylate monomers were used. 1,1,2-Trichlorotrifluoroethane was used as foaming agent. N,N-dimethyl-p-toluidine was used as initiator in amount of 0.01% by weight of the composition. The expansion coefficient data are shown in Table 4.

Table 4

Foaming compositions based on different cyanoacrylate monomers

Cyanoacrylate monomer	Volume ratio of cyanoacrylate to foaming agent	Expansion coefficient
Methyl 2-cyanoacrylate	4:1	13
Ethyl 2-cyanoacrylate	4:1	25
Butyl 2-cyanoacrylate	1:1	29
iso-Butyl 2-cyanoacrylate	1:1	35
Allyl 2-cyanoacrylate	1:1	20
2-Methoxyethyl 2-cyanoacrylate	4:3	20
2-Ethoxyethyl 2-cyanoacrylate	4:3	15
2-Methoxyisopropyl 2-cyanoacrylate	4:3	23

Example 5

Compositions based on various cyanoacrylate monomers and 1,1,2-trichlorotrifluoroethane in a volume ratio of 4:1 and containing 0.01% by weight N,N-dimethyl-p-toluidine as initiator were injected into polyethylene tubes with an internal diameter of 12.5 mm. Seconds after the injection, the composition expanded into polycyanoacrylate foam which plugged the tubes. The walls of the tubes were carefully cut and the foamed material removed. Test pieces of the foam were cut from it and tested. The results of some physical characteristics of the foams are presented in Table 5.

Table 5

Physical characteristics of polycyanoacrylate foams

2-Cyano-acrylate monomer	Specific gravity	Tensile strength at break	Elongation at break	Tensile shear strength at break	Compression strength at 10% deformation
	g/cm^3	kg/cm^2	%	kg/cm^2	kg/cm^2
Methyl	0.28	0.8	2.5	0.5	5.7
Ethyl	0.13	10.6	3.7	5.2	4.9
Butyl	0.25	5.7	6.7	1.8	4.9
iso-Butyl	0.24	3.2	3.7	3.0	5.7
Allyl	0.18	5.0	3.0	3.0	7.3
2-Methoxy-ethyl	0.41	1.6	2.0	1.9	6.5
2-Ethoxy-ethyl	0.22	1.6	1.7	1.5	5.5
2-Methoxy-isopropyl	0.28	1.8	2.0	1.7	4.0

Example 6

Tubes and pipes made of cast iron, stainless steel, copper, polycarbonate, polystyrene, polyvinylchloride, polypropylene and polyethylene having inside diameters from 1 mm to 100 mm were plugged with foam by injecting through a specially drilled opening a foaming composition consisting of ethyl 2 cyanoacrylate and 1,1,2-trichlorotrifluoroethane in a volume ratio of 4:1 and containing 0.01% by weight N,N-dimethyl-p-toluidine. The expanded foam created an efficient plug, whose adhesion to the pipe wall was higher than the strength of the foam material itself. The pipes were hermetically sealed by the foam plug and easily withstood pressure of 10 Atmospheres.

In a following operation acetone was injected with a syringe through the same opening used for injecting the composition, which subsequently was also plugged with foam. In 5 seconds to 2 minutes, depending on the size of the pipe, the foam collapsed and flow through the pipe was restored.

CLAIMS

1. A foam-forming cyanoacrylate composition comprising a 2-cyanoacrylate ester monomer, a liquid foaming agent and a polymerization initiator, for anionic polymerization of the monomer, which composition upon or after mixing polymerizes and foams to produce a polycyanoacrylate foam.

2. A composition as claimed in claim 1, wherein the cyanoacrylate monomer and the liquid foaming agent are in a volume ratio from 1:10 to 20:1.

3. A composition as claimed in claim 1 or claim 2, wherein the polymerization initiator is in an amount of from 0.00001% to 1% by weight of the composition.

4. A composition as claimed in any one of the preceding claims, wherein the foaming agent is an organic compound with a boiling point not higher than 100°C.

5. A composition as claimed in claim 4, wherein the foaming agent is miscible with the cyanoacrylate monomer.

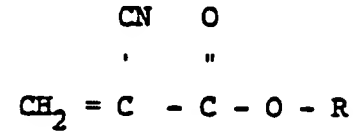
6. A composition as claimed in claim 5, wherein the foaming agent has a solubility parameter below 9 and is non-polar.

7. A composition as claimed in claim 4, wherein the foaming agent is pentane, hexane, heptane, 1,1,2-trichlorotrifluoroethane, 1,1,1-trichlorotrifluoroethane, petroleum ether, diethyl ether, cyclopentane, cyclohexane, benzene, carbon tetrachloride, chloroform, methylcyclopentane, dimethylsulfide, 1,1-dichlororethane, 1,1,1-trichloroethane,

perfluorohexane, perfluoroheptane, 1-bromopropane or a mixture thereof.

8. A composition as claimed in claim 7, wherein the foaming agent is pentane, hexane, 1,1,2-trichlorotrifluoroethane, petroleum ether, cyclohexane or diethyl ether or is a mixture thereof.

9. A composition as claimed in any one of the preceding claims, wherein the cyanoacrylate monomer comprises one or more compounds of the formula



wherein R is alkyl, cycloalkyl, alkenyl, cycloalkenyl, alkynyl, aryl or an aromatic heterocyclic radical or is one of these moieties substituted with one or more other of the moieties, and wherein these moieties may optionally be substituted with alkoxy, carbalkoxyalkyl, halogen or another inert substituent.

10. A composition as claimed in claim 9, wherein R contains from 1 to 16 carbon atoms, the heteroatom ring members of any aromatic heterocycle being counted as a carbon atom.

11. A composition as claimed in claim 9 or claim 10, wherein R is alkyl, halogenated alkyl, cycloalkyl, cycloalkylalkyl, alkylcycloalkyl, alkenyl, alkynyl, phenyl, halogenated phenyl, phenylalkyl, halogenated phenylalkyl,

alkylphenyl, halogenated alkylphenyl, alkylphenylalkyl, halogenated alkylphenylalkyl, alkoxyalkyl, alkoxyalkoxyalkyl, carbalkoxymethyl or isopropylideneglyceryl.

12. A composition as claimed in claim 11, wherein R is ethyl, n-butyl, iso-butyl, 2-methoxyethyl, 2-ethoxyethyl or 2-methoxyisopropyl.

13. A composition as claimed in any one of the preceding claims, wherein the initiator is pyridine, aminopyridine, vinylpyridine, methoxyethylpyridine, piperidine, picoline, lutidine, N,N-dimethyl-p-toluidine, N,N-dimethyl-o-toluidine, N,N-dimethyl-m-toluidine, triphenylphosphine, triethylphosphine, tribenzylamine, triethylamine, benzyldimethylamine, diethylenetriamine, benzyltriethylamine, tribenzylamine, poly(4-vinylpyridine), a calixarene, a tertiary amine-SO_3 complex, polyethyleneglycol, a phenolformaldehyde resin, vinylimidazole, triethanolaminatotitanium, an aminosilane, a phosphite, a metal acetylacetonate, N-(oxydiethylene) benzothiazole-2-sulfenamide, bismuth dimethyldithiocarbamate, an alcohol, a base or a hydroxyl or amine group containing compound.

14. A composition as claimed in claim 13, wherein the initiator is N,N-dimethyl-p-toluidine or N-(oxydiethylene) benzothiazole-2-sulfenamide.

15. A composition as claimed in any one of the preceding claims and which further comprises a free-radical polymerization inhibitor or an anionic polymerization

inhibitor in an amount insufficient to inhibit the initiator, or both.

16. A composition as claimed in any one of the preceding claims and further comprising another reactive monomer or a reactive resin or oligomer, a thickener, a viscosity regulator, a rubber, a plasticizer, a toughener, a compatibilizer, a thixotropic agent, a colourant, a deodorant or a mixture thereof.

17. A poly(2-cyanoacrylate ester) foam, the polymer optionally including a minor amount of one or more other monomer units than 2-cyanoacrylate ester units or a reactive resin or oligomer.

18. A foam as claimed in claim 17, wherein the 2-cyanoacrylate ester is as defined in any one of claims 9 to 12.

19. A method of forming a poly(2-cyanoacrylate ester) foam, comprising forming a composition as defined in any one of claims 1 to 16 and allowing the monomer to polymerize and form a foam.

20. A method as claimed in claim 19 wherein the components of the composition are mixed together in a static mixer or in a spray.

21. A kit or device for forming a poly(2-cyanoacrylate ester) foam, comprising a first container containing 2-cyanoacrylate ester monomer and a second container

containing a polymerization initiator for anionic polymerization, the kit additionally containing a liquid foaming agent in the first container, in the second container or in a third container or in any combination thereof.

22. A kit or device as claimed in claim 21, wherein the monomer is as defined in any one of claims 9 to 12, the foaming agent is as defined in any one of claims 4 to 8, the initiator is as defined in claim 13 or claim 14, the monomer and the foaming agent are in a volume ratio of from 1:10 to 20:1, and/or the polymerization initiator is in an amount of from 0.00001% to 1% by weight of the total contents of the kit.

23. A kit or device as claimed in claim 21 or claim 22 wherein the monomer is in admixture with an anionic polymerization inhibitor or a free radical polymerization inhibitor or both, and/or one or more of the containers additionally contains one or more of the further components defined in claim 16.

24. A kit or device as claimed in any one of claims 21 to 23 which comprises a two part or three part syringe.

25. A kit or device as claimed in any one of claims 21 to 23 wherein the first and second containers and any third container are connected by ducts to a spray head for mixing the contents of the containers and means is provided to expel the contents of the containers through the ducts to the spray head.

26. A delivery system for forming a composition as defined in any one of claims 1 to 16 the system comprising the monomer and the initiator in separate containers from which they may be dispensed, the foaming agent being included in said containers and/or in a separate container, and the system optionally including means to mix the container contents before or as they are dispensed from the system.

27. A preblend for forming a cyanoacrylate foam, comprising a 2-cyanoacrylate ester monomer and a liquid foaming agent.

28. A preblend as claimed in claim 27, wherein the cyanoacrylate monomer and the foaming agent are in a volume ratio of from 1:10 to 20:1, the foaming agent is as defined in any one of claims 4 to 8 and/or the cyanoacrylate monomer is as defined in any one of claims 9 to 12.

29. A preblend as claimed in claim 27 or claim 28 and which further comprises a free-radical polymerization inhibitor, an anionic polymerization inhibitor or both, and/or one or more further components as defined in claim 16.

30. A method of blocking a pipe, comprising placing in the pipe a composition as defined in any one of claims 1 to 16 and allowing the composition to polymerize to form a foam which blocks the pipe.

31. A method as claimed in claim 30, wherein the pipe is blocked temporarily and is subsequently unblocked by applying to the foam a solvent therefor.

32. A method of forming a cast, for example for a broken or injured limb, comprising applying a composition as defined in any one of claims 1 to 16 to the limb or other body around which the cast is to be formed and allowing the composition to polymerize and foam to form a cast.

33. A method of occluding or stopping a blood vessel, fallopian tube or other tubular part of a human or animal body, comprising applying to the tubular part a composition as defined in any one of claims 1 to 16 and allowing the composition to polymerize to form a foam occluding to stopping the tubular part.

34. The use of 2-cyanoacrylate ester monomer as a starting material to form a polycyanoacrylate foam.

35. The use of claim 34 wherein the monomer is as defined in any one of claims 9 to 12.

36. The use of an organic liquid with a boiling point of no greater than 100°C as a foaming agent to form a polycyanoacrylate foam.

37. The use of claim 36 wherein the organic liquid is as further defined in any one of claims 6 to 8.

38. A composition as defined in any one of claims 1 to 16 for use in the treatment of the human or animal body by surgery or therapy.

39. A method of forming a polymer foam on or around a part of the human or animal body, comprising applying a composition as defined in any one of claims 1 to 16 on or around the part.